Determining Aerosol Mean Residence Times and Black Carbon Washout Rates with Natural Radionuclides and Isotopic Signatures

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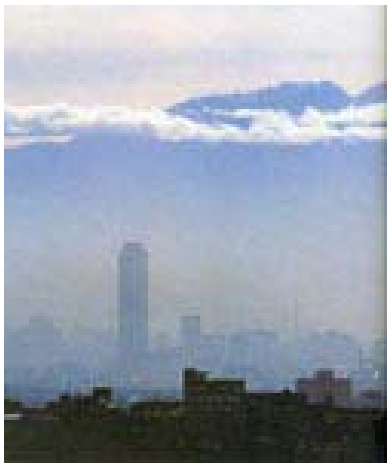
Aerosol Radiative Forcing – You Need to Determine:

Optical Properties -(Size, Chemical Composition as Function of Size, Optical Constants, Etc.)

Sources - (Natural and Anthropogenic) ←

Lifetimes - (Size and Hygroscopicity) ←

Position in Atmosphere (Vertical & Horizontal Distributions)



Mexico City – MEGACITY MAJOR SOURCES

Project Objective

Make use of naturally occurring radionuclides and stable isotopic signatures to determine the sources, removal and transport processes, and atmospheric lifetimes of fine carbonaceous aerosols.

Methods – Lifetimes – FIELD STUDIES:

Impactors to collect size-fractionated interstitial fine (submicron) aerosols.

Precipitation samples collected simultaneously and analyzed for black carbon (BC) and organic carbon (OC) contents to determine the efficiency of washout.

Residence times of size-fractionated fine aerosols - relative amounts of the attached natural radionuclide tracers ^{7}Be, ^{210}Pb, ^{210}Bi, and ^{210}Po.

Estimate atmospheric ages of interstitial aerosols and aerosols in precipitation samples.

METHODS - SOURCES

Total ^{7}Be and ^{210}Pb contents - estimate of the amount of aerosol originating from upper-air transport.

$^{13}C/^{12}C$ and $^{15}N/^{14}N$ data to assess aerosol source signatures

^{14}C data to determine fossil and biogenic source contributions directly.

^{14}C – Marker of Biogenic Input

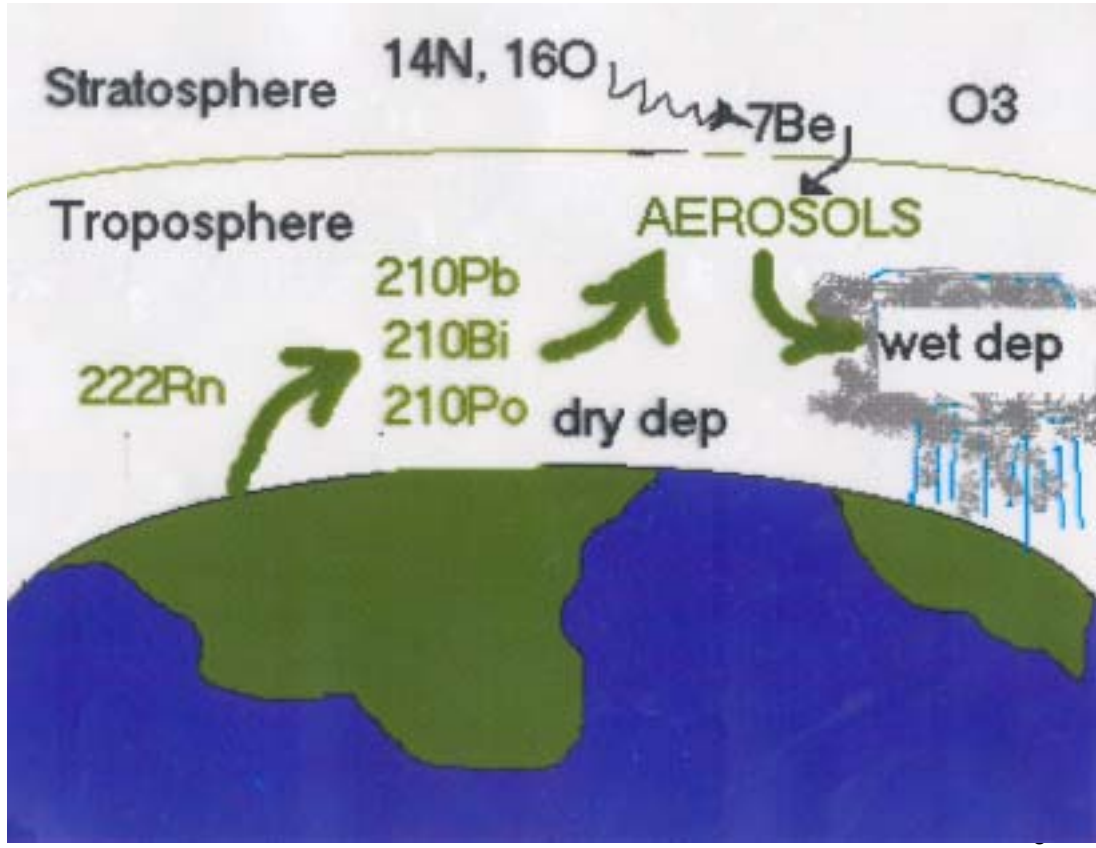
Fossil Carbon - Oil and Petroleum – Zero ^{14}C

^{40}K in submicron aerosol as marker for wood smoke

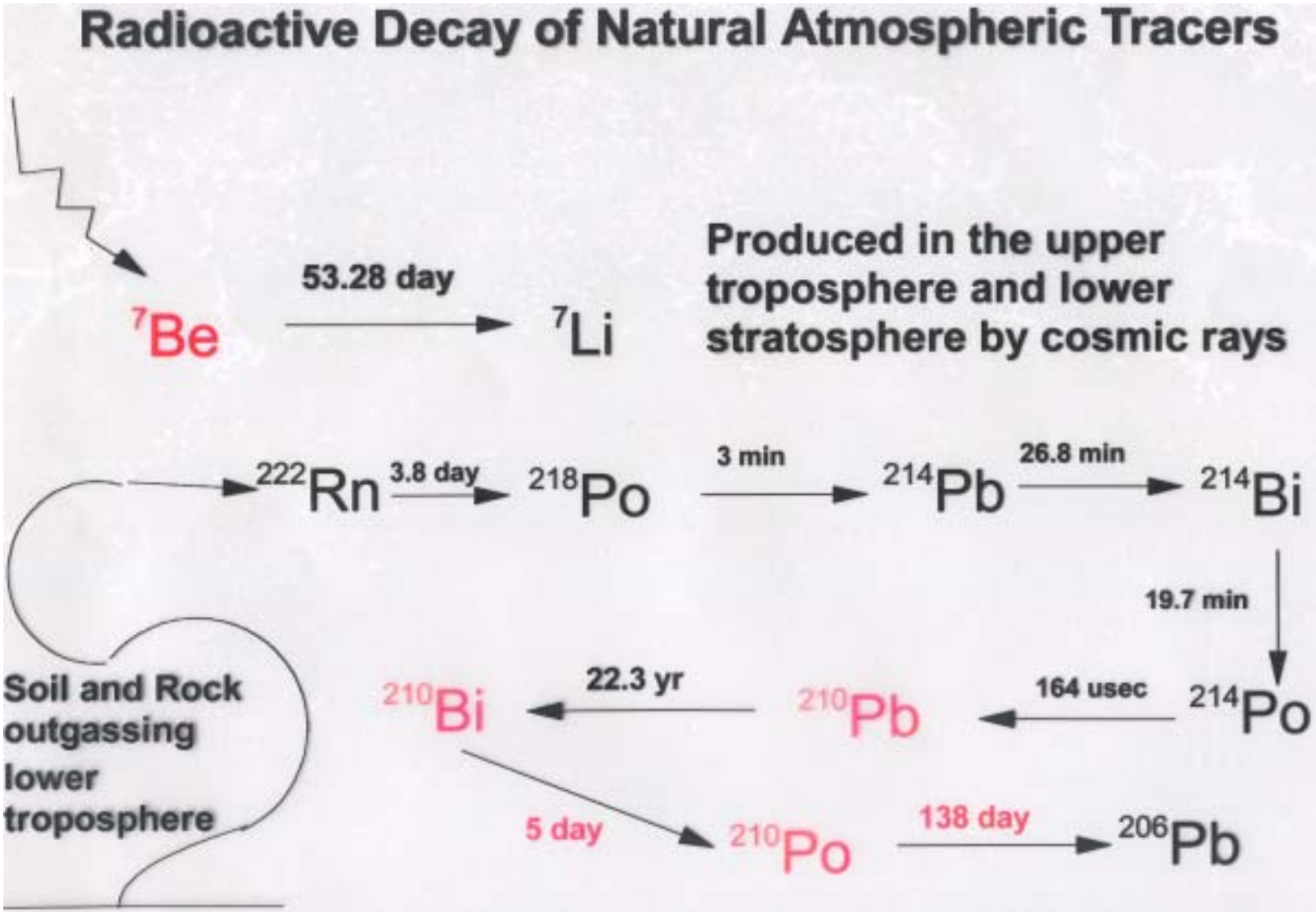
University of Illinois, Chicago and CAMS Collaboration

Natural Radionuclides To Aid in Determine Washout Rates

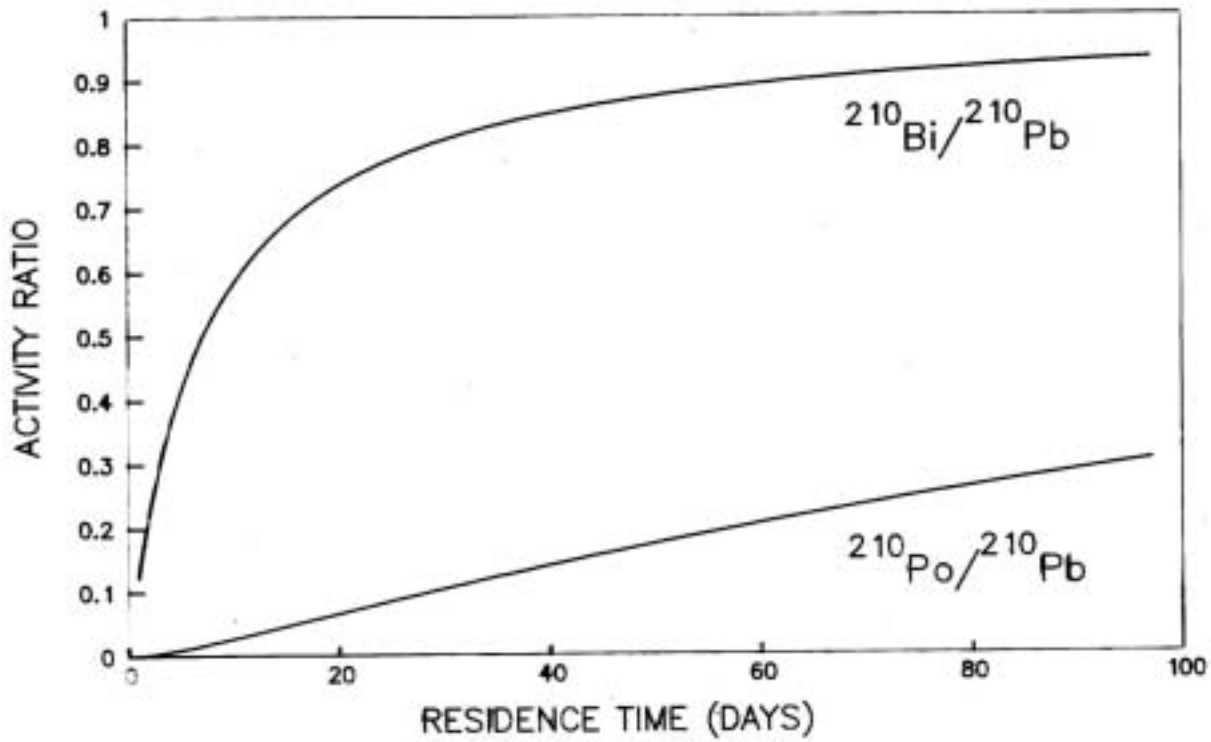
Natural Radionuclides ^{7}Be, ^{210}Pb, ^{210}Bi, ^{210}Po all attach to fine aerosol fraction 0.1-0.6 μ m



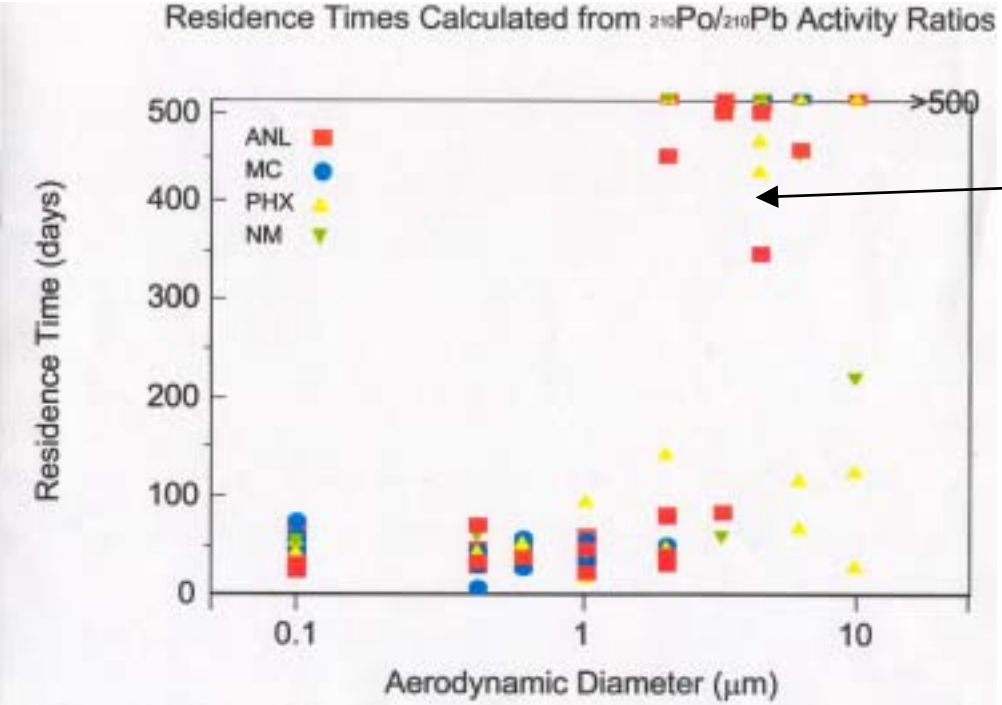
Radioactive Decay of Natural Atmospheric Tracers



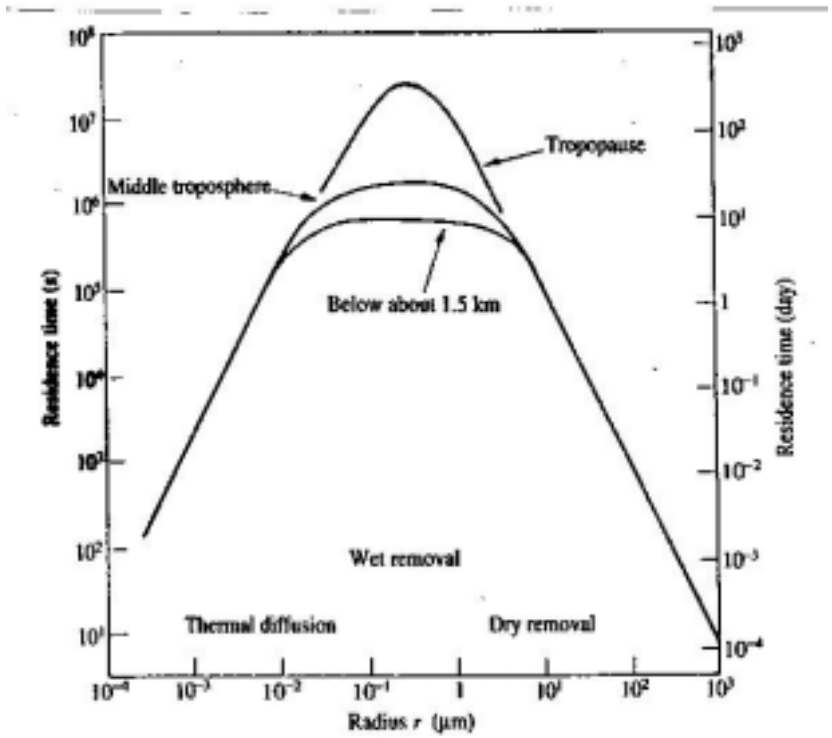
Activity Ratio vs Residence Time for Aerosols Removed in Precipitation



(adapted from Nevissi, A.E. 1991, J. Radioanal. Nucl. Chem.)



Windblown dust and soil Contamination – old!



MODELED AEROSOL LIFETIMES INCREASE WITH ALTITUDE

Jacobs Group – INDOEX results, Etc.

RECENT RESULTS FOR PITTSBURGH (Gaffney, Nancy A. Marley, and Mary M. Cunningham, "Natural radionuclides in fine aerosols in the Pittsburgh area." *Atmospheric Environment*, 38, 3191-3200 (2004).)

URBAN AREAS – AGES RANGE FROM 10-50 Days

Apparent Ages for Aerosols – NETL

Sample	SIZE(μm)	CORR. AGE (days)
PA1	<1	17
PA2	>1	11
PA5	<1	19
PA6	>1	20
PA9	<1	21
PA10	>1	12
PA11	<1	18
PA12	>1	15
PA13	<1	30
PA14	>1	27
PA17	<1	10
PA18	>1	30
PA21	<1	12
PA22	>1	25
PA25	<1	24
PA26	>1	32
PA29	<1	31
PA30	>1	46

OK SO WHAT IS CAUSING THIS?

–PRECIPITATION - WASHOUT

– SULFATE, NITRATE- Soluble - 10 Days

(Gaffney, et.al, "Measurement of ^{7}Be and ^{210}Pb in Rain, Snow, and Hail." *J. Applied Meteor.* **33** 869-873 (1994).)

> **10 Days Aerosol Lifetimes!**

Something Hydrophobic- Less Soluble

BLACK CARBON?

SIMPLE LABORATORY STUDIES

ULTRAFILTERED RAINWATER

Add – NBS Standard Diesel Soot

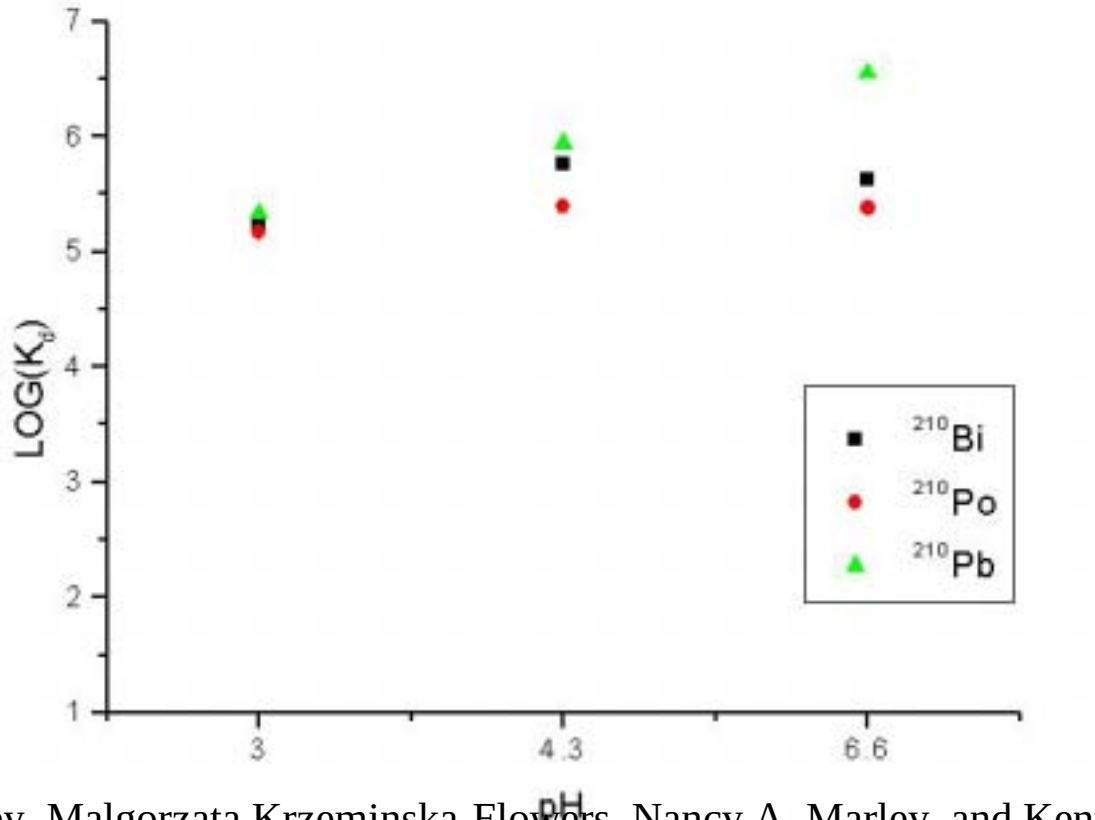
Add – Low level of Natural Radioactive Tracer at known pH (i.e. ^{7}Be, ^{210}Pb, ^{210}Bi, ^{210}Po)

Look at Distribution

K_d = Activity on Carbon Soot/Activity in Water

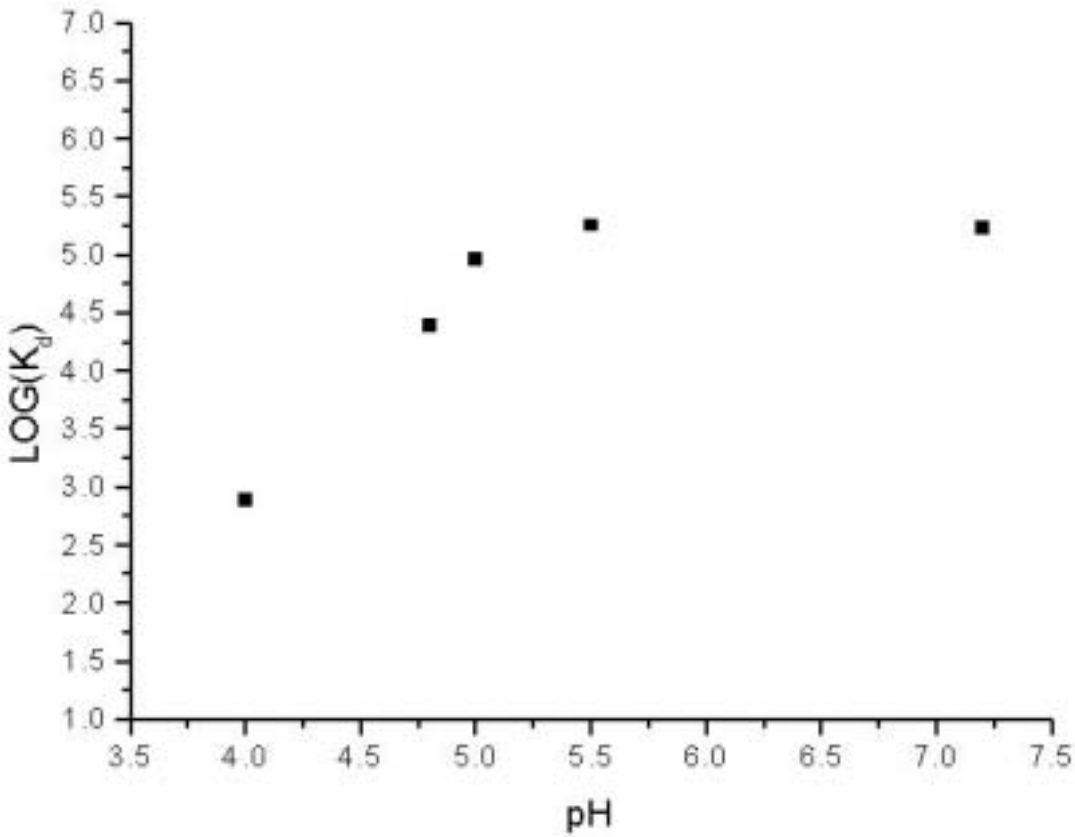
normalized to the mass of carbon and the water volume

K_d for ^{210}Pb and its daughters on untreated soot as a function of pH.



158. Jeffrey S. Gaffney, Malgorzata Krzeminska-Flowers, Nancy A. Marley, and Kent A. Orlandini, "Rainwater Interactions with Natural Radionuclides on Carbonaceous Soot." Seventh Conference on Atmospheric Chemistry as part of the 85th American Meteorological Society (AMS) Annual Meeting in San Diego, California 9-13 January 2005, Paper 2.2 CD Preprint Volume, 3p. (2005).

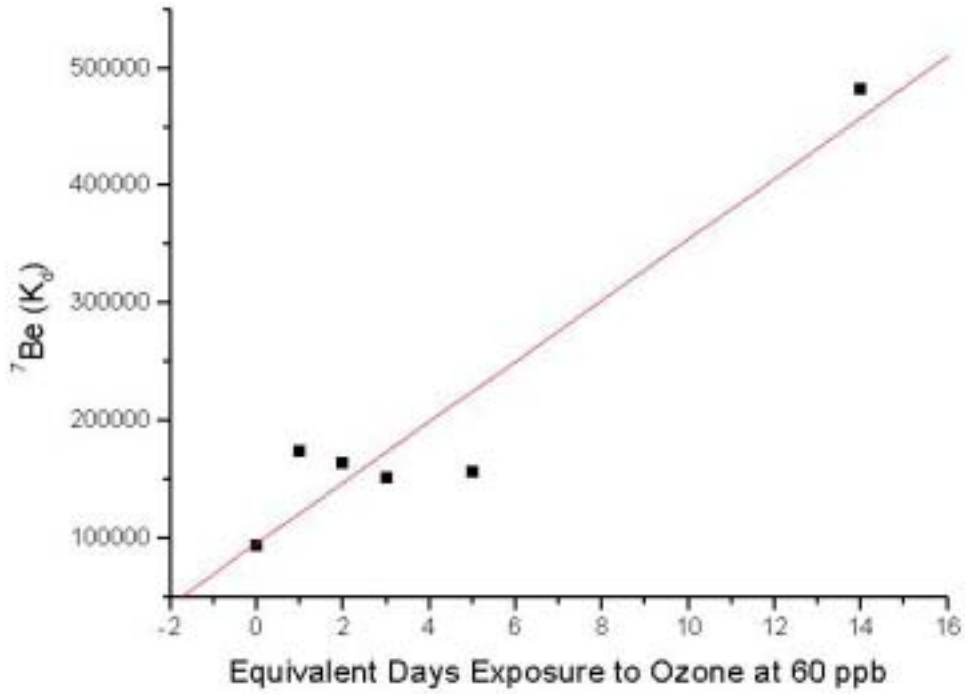
Log K_d vs pH plot for ^{7}Be attachment to untreated soot in rainwater.



Black Carbon – AGING EXPERIMENT

Expose BC to Ozone Equivalent Amounts – Assuming Ozone 60 ppb

Look at Kd vs Ozone – BC Exposure Periods



FIELD MEASUREMENTS – Preliminary Results

DRY COLLECTOR – ONLY COLLECTS AIR WHEN NO PRECIP.

WET COLLECTOR – TIED TO PRECIP
COLLECTOR –

ONLY COLLECTS AIR WHEN IT IS PRECIPITATING

Interstitial aerosol (2.5 micron cut off) or Cascade Impactor

Data for two periods of wet and dry sampling high volume samplers Dry (D) or Wet (W) sampling periods and rain water associated ^{7}Be activity and volumes at Argonne National Laboratory site.

	Julian Days	Dry or Wet	Volume m^3	mBq m^{-3}	Rain (ml)	Rain Bq L^{-1}
	160-163	Dry	1570	1.99	-	-
	163-165	Dry	2738	1.57	-	-
Convective Storm	163-165	Wet	1305	1.88	2200	0.18
	165-167	Dry	2372	2.09	-	-
	166-167	Dry	869	1.88	-	-
Frontal Passage Event	166-167	Wet	203	0.21	4600	0.32
	167-173	Dry	5469	0.47	-	-

CONCLUDING REMARKS

PRELIMINARY RESULTS – VERY PROMISING -RADIONUCLIDES ARE ATTACHED STRONGLY TO SOOT!

MAY BE ABLE TO SEPARATE SOOT AND AGE DATE.

RESULTS FOR ^{7}Be CONSISTANT WITH OTHER RESULTS INDICATING ^{7}Be NOT READILY WASHED OUT – UPPER ATMOSPHERIC AEROSOLS – BC?

IMPORTANT MODELING IMPLICATIONS – NOT ALL AEROSOLS WASHOUT EVERYTIME IT RAINS

WILL ALSO BE COUPLING THIS WORK TO ^{14}C MEASUREMENTS IN DOE ASP FUTURE WORK.

^{14}C on Total Organic Aerosol in PM <1 micron – Mexico City indicate Strong Biogenic Source – Long Range Transport/Trash Burning

Acknowledgements.

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